# Chemical Bond Between Stabilizers and HTPB Binders in Propellants

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**Chemische Bindung zwischen Stabilisatoren und dem HTPB-Binder in Treibstoffen**

Die Bildung einer chemischen Bindung zwischen Stabilisatoren und dem Isocyanat-Binderteil in HTPB-Bindern wurde nachgewiesen. Ziel war, eine Erklärung zu finden, warum es nicht möglich ist, einige bestimmte Stabilisatortypen aus den Treibstoffen von Raketenmotoren zu extrahieren. Die Untersuchungen wurden mit der $^1$H-NMR-Spektroskopie an verschiedenen Kombinationen zwischen Stabilisatoren und den zur Härtung von HTPB-Bindern verwendeten Isocyanaten durchgeführt. Es konnte gezeigt werden, daß einige dieser Stabilisatoren an das polymere Netzwerk über das Diisocyanat chemisch gebunden werden. Richtlinien zur Beurteilung einer möglichen Anbindung eines Stabilisators an den Binder werden abgeleitet. Schließlich wird eine Auswirkung der Anbindung des Stabilisators auf seine stabilisierende Wirkung diskutiert.

**Liaison chimique entre les stabilisants et les liants PBHT dans les propulsifs**

La formation de liaisons chimiques entre le stabilisant et l'isocyanate a été caractérisée dans un liant à base de polymère PBHT. L'étude a pour but d'expliquer l'impossibilité d'extraire certains stabilisants du liant dans les moteurs fusée. Les expériences on été effectuées par spectroscopie RMN-$^1$H avec diverses combinaisons de stabilisants et d'isocyanates utilisées pour cuire le PBHT. Il a été démontré que certains stabilisants utilisés dans les propulsifs pour fusées sont attachés au réseau polymérique du liant par l'entremise d'une réaction avec l'isocyanate. Les critères pour déterminer la possibilité d'un stabilisant à se lier au réseau sont décrits. Finalement, l'implication de la liaison chimique sur l'effet stabilisant est discutée.

## Summary

The character of the chemical bond between stabilizers and isocyanates used to cure the HTPB binder was determined. The aim was to explain, why it is not possible to extract some stabilizers from the binder of rocket motors. Investigations were performed by $^1$H-NMR-spectroscopy on various combinations of stabilizers and isocyanates used to cure HTPB. It was demonstrated that stabilizes of some type can be attached to the polymeric network via a reaction with the diisocyanate. Criteria to evaluate the possibility of bonding the stabilizer to the network are derived. Finally the implication of the chemical bonding on the stabilizing effect is discussed.

## 1. Introduction

The evaluation of the propellant's degradation is a subject of interest for service life assessment of rocket motors inventories. Presently, the life cycle assessment program[1,2] performed at the Defence Research Establishment Valcartier (DREV) comprises the following analysis: measurements of the mechanical properties (modulus, ultimate tensile and compression strength), ballistic properties evaluations and chemical analysis of the ingredients (stabilizer depletion, plasticizer diffusion, crosslink density changes of the binder). As suggested by Caulder and Hernandez[3] the scanning electron microscopy (SEM) analysis of composite motors should also be integrated in a life cycle assessment program. For the chemical aspect of this program it is well recognized that the presence of stabilizers in propellants such as double base[4−8] and composites[9−11] are of primary importance for the long term chemical durability of the motors. In fact, for a double base propellant the main function of the stabilizers (namely nitro scavengers) is to trap the undesired nitrogen oxide radical species, while for composite motors the function of the stabilizers (namely antioxidants) is to trap the oxygen based radical species that otherwise lead to undesired additional crosslinking. Consequently, it is known that stabilizer analysis may give information about the degradation state of the motor. The common analytical procedure is to firstly perform solvent extraction of stabilizers or of their derivatives. Then the extracted stabilizer is quantified by analytical instruments such as the High Performance Liquid Chromatography (HPLC)[12−14]. For composite motors, we found in some cases that the stabilizers (antioxidants) were not extractable by any common organic solvents. In these situations the determination of antioxidant concentration in the rocket motor would need other innovative methods as recently suggested by Sandén et al.[15]. Nevertheless, it is important to understand the chemical phenomenon leading to the problem of the nonsoluble antioxidants.

We have performed a study which will explain for the nonsoluble antioxidants the interaction between the stabilizer, the isocyanate and the hydroxy-terminated polybutadiene (HTPB) used during the formulation of composite rocket motors. The $^1$H-nuclear magnetic resonance spectroscopy (NMR) was used to follow the chemical changes occurring between the main ingredients. The stabilizers

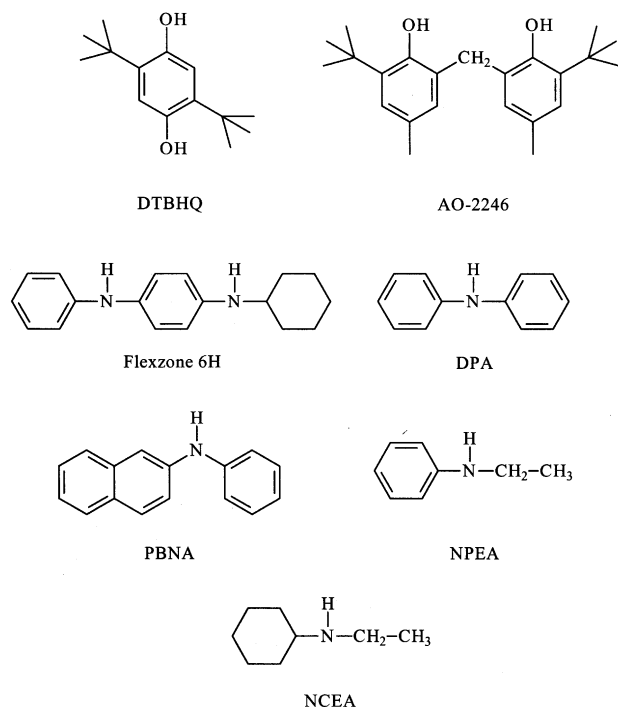* Corresponding author; e-mail: sylvain.desilets@drev.dnd.ca

**Figure 1.** Structures of the various stabilizers used for the study.

used for this study are shown in Figure 1 and cover the two main families: the phenolic stabilizers such as 2,5-di-*tert*-butyl-hydroquinone (DTBHQ) and 2,2-methylene-bis(4-methyl-6-*tert*-butyl-phenol) (AO-2246) and the amino stabilizers such as N-phenyl-N′-cyclohexyl-*p*-phenylene-diamine (Flexzone 6H), diphenylamine (DPA), phenyl-*beta*-naphthylamine (PBNA). N-phenylethylamine (NPEA) and N-cyclohexylethylamine (NCEA) were used as amino reference compounds and will lead to a better understanding of the studied phenomenon. The two main classes of isocyanates were also covered in the study: the aliphatics HMDI (hexamethylene-1,6-diisocyanate), IPDI (isophorone diisocyanate), DDI (dimeryl diisocyanate) and the aromatics TDI (toluene diisocyanate (isomeric mixture)), MDI (methylene di-4,4′-phenylisocyanate). These ingredients were reacted with a HTPB polymer to reproduce chemical reactions that take place in a formulation process.

## 2. Experimental

The NMR study of the interaction between the stabilizer and the ingredients was performed by using the following procedure: 5 g of HTPB having a molecular weight of 2800 and an equivalent weight of 1180 was mixed with 2% of the stabilizer. The presence of 2% of stabilizer was used as opposed to 0.2% in common polymer formulations in order to be easily detected in the NMR spectra. The isocyanate was then added to the mixture at a NCO/OH ratio of 0.8 to get a cured polymer having a low crosslink density. Thereby the cured polymer having a low crosslink density was soluble enough in organic solvent to perform the $^1$H-NMR study in

solution. Dibutyltin dilaurate catalyst was added at 0.05% to accelerate the curing reaction. Curing reactions were made at 50°C for a period of 48 h. As suggested by Govindan and Athithan[16] as well as by Kincal and Özkar[17], the reaction was determined to be completed by observing the disappearance of the isocyanate band (at 2250 cm$^{-1}$) in the IR spectra. The cured polymers were then studied by $^1$H-NMR in CD$_2$Cl$_2$ solvent.

A reaction between Flexzone 6H and an excess of DDI was made by using 0.2 g of Flexzone 6H (1 eq) and 0.45 g of DDI (2 eq) dissolved in 10 ml of dichloromethane at room temperature for 48 h. The mixture was extracted with a 10%-aqueous HCl solution. The reaction product present in the aqueous acidic phase was regenerated by neutralization at pH = 12 with NaOH. The resulting basic solution containing the reacted Flexzone 6H was extracted with dichloromethane which was evaporated before the analysis by $^1$H-NMR spectroscopy.

Solvent extractions were performed by using continuous extraction procedures (Soxhlet extraction for 48 h) on five cured samples having 1% stabilizer in a HTPB/isocyanate/curing catalyst formulation with a NCO/OH ratio of 1.2. DDI was used as curing agent for the five samples. The difference between the five HTPB binders was the nature of the stabilizer: 1) DTBHQ, 2) AO-2246, 3) Flexzone 6H, 4) DPA and 5) PBNA. The percentage of the stabilizers recovered during the extractions was then quantified with $^1$H-NMR by using a known quantity of an internal standard (1,1,2,2-tetrachloroethane) having a single peak at 6.2 ppm in the spectrum. In order to get precise integrations of the signals the acquisition of the spectra was performed with a relaxation delay of 120 s between each scan.

## 3. Results and Discussion

The first experiment leading to this study came from an attempt[1,2] to identify and to quantify the presence of the stabilizer in a Sidewinder rocket motor having Flexzone 6H as antioxidant. In this case, the chemical analysis of the stabilizer was attempted many times by using a continuous extraction procedure of the propellant in dichloromethane (Soxhlet extraction for 48 h). The extracted solution was then analyzed by HPLC using reversed phase technique (Spherisorb ODS-2, 250 mm × 4.6 mm) and a mobile phase consisted of acetonitrile/water (62/38) which contained 1% (v/v) triethylamine. The triethylamine was used to give a sharp peak from the Flexzone 6H stabilizer in order to neutralize the unwanted affinity of the amino functions of Flexzone 6H (leading to a very broad peak) with the packing of the HPLC column. By using this procedure, it was found[1,2] that Flexzone 6H was not extractable from the rocket motor by organic solvents. Additional experiments by $^1$H-NMR spectroscopy also confirmed the absence of Flexzone 6H in the extracted mixture. By comparison with Sidewinder rocket motors containing AO-2246, it was found[1,2] that in this case the antioxidant was extractable

and analyzable by HPLC. Consequently it was suspected for the motor containing Flexzone 6H that this antioxidant may have reacted with the isocyanate during the fabrication process of the motors. That would explain why the antioxidant was not extractable by any procedure.

To confirm this assumption, a NMR study was performed firstly by reacting Flexzone 6H and DDI in excess with a NCO/Flexzone 6H ratio of two. Two is the exact stoichiometric ratio that could lead to a complete reaction between the isocyanate and the two amino groups of Flexzone 6H. A comparison between the $^1$H-NMR spectra of pure Flexzone 6H (Figure 2a) with the spectra of the mixture of Flexzone 6H and DDI (Figure 2b) shows that the antioxidant strongly reacted with the isocyanate after 48 h. In fact, by comparison with Figure 2a, the spectra on Figure 2b show a strong spectral shifting of H-6 and H-5 resulting from the reaction between Flexzone 6H and DDI. The reacted Flexzone 6H has two triplet signals from H-6 located at 4.4 ppm and 3.9 ppm
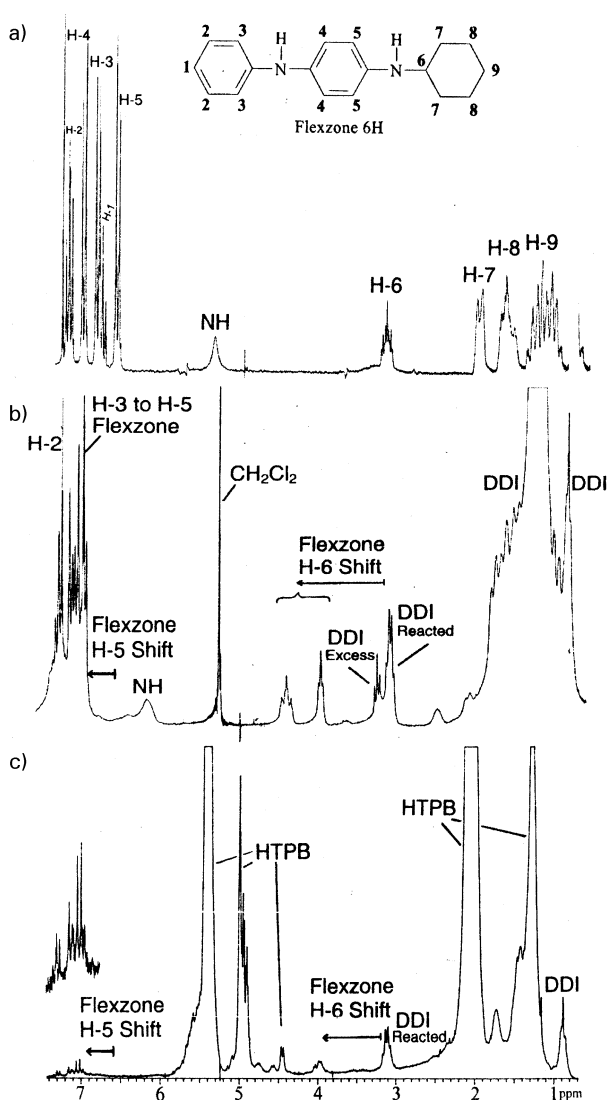
in the spectrum. These two signals are readily attributed to the two isomeric forms of the unsaturated six-membered ring of Flexzone, namely the axial and the equatorial conformations. This result shows with evidence that the major structural changes of Flexzone 6H is specifically located on the second amino function (beside H-6) as described in Figure 3. The nonreacted excess of isocyanate present at 3.2 ppm in Figure 2b shows that the first amino group (between H-3 and H-4) is much less reactive toward isocyanates and is consequently not touched. The $^1$H-NMR spectroscopy of HTPB cured with DDI (NCO/OH = 0.8) and Flexzone 6H was finally performed and shows in Figure 2c the same reaction effect as observed previously. It also demonstrated that the amino function of Flexzone 6H is more reactive toward isocyanates than the primary hydroxyl group of HTPB. Consequently it was concluded that Flexzone 6H antioxidant was strongly attached to the molecular chain end of the HTPB network by a covalent chemical bond, as described in Figure 3. Now it is conceivable that a such reaction also occurs in rocket formulations as supported by the difficulty to extract the antioxidant in the case of the Sidewinder motors having Flexzone 6H.

Knowing that some stabilizers may be chemically attached with the binder, a study of the stabilizer reactivity toward the isocyanates in the presence of HTPB was performed by using the same $^1$H-NMR spectroscopy methodology as for Flexzone 6H. In fact, the stabilizers that did not react with isocyanates had no spectral modifications of their NMR signals. Various combinations of isocyanates and stabilizers cured with HTPB were performed. The overall results are summarized in Table 1. A "Yes" in the table means that the stabilizer was attached to the polymeric network. Basically, it shows for a binder with NCO/OH = 0.8 that the stabilizers containing phenolic structures (such as DTBHQ, AO-2246 ) as well as diphenylamine structures (such as DPA, PBNA) are not attached to the polymeric network. Only amino structures having one or two aliphatic groups on the amino function (Flexzone 6H, NPEA, NCEA) are very reactive toward all types of isocyanates. However, this NMR study was performed without an excess of isocyanates. In a more realistic situation the large excess of isocyanate (NCO/OH = 1.2) may react with the stabilizer in competition to the formation of biuret and/or allophanate crosslink functions[18].



**Figure 2.** $^1$H-NMR spectral results for Flexzone 6H stabilizer (a) Pure Flexzone 6H, (b) Flexzone 6H reacted with DDI, (c) Flexzone 6H reacted with DDI and HTPB.
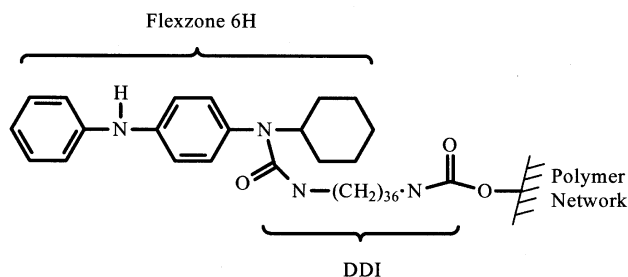


**Figure 3.** Structure of Flexzone 6H stabilizer linked to the HTPB polymeric network.

**Table 1.** Existing Chemical Bond Between Stabilizers and HTPB Cured with Various Isocyanates (with NCO/OH = 0.8 and 2% Stabilizer)

| Stabilizers | HMDI | IPDI | DDI | TDI | MDI |
|---|---|---|---|---|---|
| DTBHQ | NO | NO | NO | NO | NO |
| AO-2246 | NO | NO | NO | NO | NO |
| Flexzone 6H | **YES** | **YES** | **YES** | **YES** | **YES** |
| DPA | NO | NO | NO | NO | NO |
| PBNA | NO | NO | NO | NO | NO |
| NPEA | YES | YES | YES | YES | YES |
| NCEA | YES | YES | YES | YES | YES |

In order to get a better picture in the case of a crosslinked binder, some extractions were performed on five HTPB binders each having a different stabilizer. All binders had a NCO/OH ratio of 1.2 (as opposed to NCO/OH ratio of 0.8 for the NMR study). By such experiments it may be concluded that the extracted stabilizers were not attached to the polymeric network. The results are resumed in Table 2 and confirm for Flexzone 6H the presence of the strong chemical bond with the polymeric network. For DTBHQ the presence of an excess of isocyanate (NCO/OH = 1.2) has also led to a chemical bond with the binder (74%) while AO-2246 was partly attached to the polymeric network (24%). DPA and PBNA were easily extractable and almost not touched (less than 5%) as observed in other propellant types[19]. For DPA most of the weight loss observed was attributed to the natural volatility of this stabilizer at 50 °C. Such weight loss for DPA evaluated to 7−12% after 48 h has been subtracted to get the result given in Table 2. Consequently, Table 2 can be used as a reference guide to evaluate if the stabilizer will be free in the formulation and consequently extractable by an organic solvent. AO-2246 was less reactive toward isocyanates than DTBHQ because of the presence of an internal hydrogen bonding between the two OH functions present in AO-2246.

Knowing that some stabilizers are being attached to the binder, they may be seen as stabilizers which have not survived the curing process, as suggested by Davis et al.[9]. Such an effect will evidently reduce the mobility of the stabilizer in a composite propellant matrix. Also by being linked to the amino group for example, it has the effect of changing the chemical structure of the stabilizer. Consequently it raises the possibility that the stabilizing effect of the reactive stabilizers (Flexzone 6H for example) may be reduced by one of these two effects. Chevalier et al.[20] reported in a study by Differential Scanning Calorimetry (DSC), that the stabilizing effect of Flexzone 6H for HTPB cured with a monoisocyanate was still present. However, the

**Table 2.** Percentage of the Stabilizer Attached to the HTPB Polymeric Network (with NCO/OH = 1.2 and 1% Stabilizer)

| Stabilizers | % Attached |
|---|---|
| DTBHQ | 74% |
| AO-2246 | 24% |
| Flexzone | 100% |
| DPA | < 5% |
| PBNA | < 5% |

use of a monoisocyanate in that study could not lead to the formation of the chemical bond that we observed between the stabilizer and the polymeric network. Nevertheless, Duchesne[21] reported data on the effectiveness of various stabilizers during aging process of composite propellants with NCO/OH = 0.85 at 60 °C after 56 days. These results were based on mechanical property changes of the HTPB composite propellants and showed that Flexzone 6H as well as Flexzone 7L provided efficient protection against oxidation. In fact, the diphenylamine part of the Flexzone structure remains intact (see Figure 3) and consequently still acts as a stabilizer. For DTBHQ he also reported[21] an efficient protection against oxidation but, as we now know at a NCO/OH ratio of 0.85, DTBHQ is not attached to the binder. As shown in literature[15], it is obvious that the OH functions of the phenolic antioxidant (DTBHQ or AO-2246) have to be free in the binder to participate to the stabilizing effect. Thus, the DTBHQ attached to the network will never be very effective. In this case, a larger quantity (an excess) of the stabilizer in the formulation or a lower NCO/OH ratio ( < 1.0) would be necessary.

## 4. Conclusions

The results show that amino stabilizers having one or two aliphatic groups attached to the amino function (such as Flexzone) are very reactive toward isocyanates and consequently attached to the cured binder. In some conditions, the phenolic stabilizers may also be attached to the polymeric network (24% for AO-2246 and 74% for DTBHQ). However, stabilizers with diphenylamine type structures (DPA, PBNA) were not found to be attached to the polymeric network and so considered to be free in the binder. These results show that stabilizers reactive toward isocyanates are not extractable from the rocket motor by any procedure. The chemical bond between the stabilizer and the polymeric network does not seem to reduce the stabilizing efficiency of Flexzone. However, for phenolic stabilizers the non extractable portion observed is probably not effective against the oxidation process.

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